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DEVELOPMENT OF METHOD FOR NTA ANALYSIS IN RAW WATER

J. K. Taylor, et al

National Bureau of Standards

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Development of Method for NTA Analysis in Raw Water

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EPA-R2-72-057
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DEVELOPMENT OF METHOD FOR NTA ANALYSIS IN RAW WATER

By

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Project 16020 GVY

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DEVELOPMENT OF METHOD FOR NTA ANALYSIS IN RAW WATER,

Taylor, J. K.; Zielinski, W. L., Jr.; Maienthal, E. J.; Durst, R. A.; Burke, R. W.

National Bureau of Standards, Washington, D.C.

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The free acid form of nitrilotriacetic acid is readily esterified by N,O-bis(trimethylsilyl)acetamide and gas chromatographic analysis is directly applicable to this derivative. The response characteristic of NTA-trisilylester was 2,200 sq mm peak area per microgram of NTA at maximum sensitivity of the hydrogen flame ionization detector. Accordingly, gas chromatography has the potential for detecting NTA concentrations of practical interest providing that suitable NTA isolation techniques can be developed. The cupric ion-selective electrode provides the basis for a sensitive electrochemical detector for NTA. Apparatus for the on-stream determination of uncomplexed NTA has been developed. This may be used for determination of total NTA, after the latter is separated from bound metal ions and other complexing agents by a suitable means, such as ion-exchange chromatography. Polarographic studies have shown that the bismuth-NTA complex is a suitable method for the determination of NTA in most waters. While some metal ions may interfere, a pre-electrolysis step and/or a standard addition technique seems feasible to eliminate this problem. Potentiometric titration with cupric ion should provide a rapid and reliable referee method for the determination of NTA in detergent formulations. Such a method would appear to be superior to the spectrophotometric methods presently used, since the latter are affected by turbidities which are encountered in many of the samples. (Holoman-Battelle)

*Nitrilotriacetic acid, *Methodology, *Water analysis, *Polarographic analysis, *Pollutant identification, Chemical analysis, Lead, Cadmium, Detergents, Gas chromatography, Reliability, Turbidity, Electrochemistry, Waste identification, Copper, Ions, Organic acids,

*Ion selective electrodes, *Potentiometric titration, *Flame ionization gas chromatography, *Trace levels, Metal-NTA complexes, Bismuth, Chemical interference, Sensitivity, Ionic interference, N O-bis(trimethylsilyl)acetamide, Chelated metals

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ABSTRACT

The free acid form of nitrilotriacetic acid is readily esterified by N,O-bis(trimethylsilyl)acetamide and gas chromatographic analysis is directly applicable to this derivative. The response characteristic of NTA-trisilylester was 2,200 mm^2 peak area per microgram of NTA at maximum sensitivity of the hydrogen flame ionization detector. Accordingly, gas chromatography has the potential for detecting NTA concentrations of practical interest providing that suitable NTA isolation techniques can be developed.

The cupric ion-selective electrode provides the basis for a sensitive electrochemical detector for NTA. Apparatus for the on-stream determination of uncomplexed NTA has been developed. This may be used for determination of total NTA, after the latter is separated from bound metal ions and other complexing agents by a suitable means, such as ion-exchange chromatography.

Polarographic studies have shown that the bismuth-NTA complex is a suitable method for the determination of NTA in most waters. While some metal ions may interfere, a pre-electrolysis step and/or a standard addition technique seems feasible to eliminate this problem.

Potentiometric titration with cupric ion should provide a rapid and reliable referee method for the determination of NTA in detergent formulations. Such a method would appear to be superior to the spectrophotometric methods presently used, since the latter are affected by turbidities which are encountered in many of the samples.

This report was submitted in fulfillment of Project 16020 GVY under the sponsorship of the Water Quality Office, Environmental Protection Agency.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Gas Chromatographic Studies	7
V	Ion-Selective Electrode Studies	15
VI	Polarographic Studies	19
VII	Potentiometric Titration Studies	23
VIII	Acknowledgements	25
IX	References	27

SECTION I

FIGURES

No.		Page
1	Gas Chromatographic Apparatus	8
2	Derivatization of Nitrilotriacetic Acid	9
3	Gas Chromatogram of Tri-Ester Derivative	10
4	Gas Chromatography-Mass Spectrometry System	11
5	Mass Spectrum of Silylated NTA	12
6	Gas Chromatographic Response for NTA	14
7	General View of Ion-selective Electrode Apparatus	15
8	Close-up View of Ion-selective Electrode Detector	16
9	Diagramatic View of Ion-selective Electrode Detector	17

TABLES

No.		Page
1	Retention Times Comparison of Silylated NTA and Fatty Acids	13
2	Apparent NTA Content of Various Detergents	24

SECTION I

CONCLUSIONS

The free acid form of nitrilotriacetic acid is readily esterified by N,O-bis(trimethylsilyl)acetamide and gas chromatographic analysis is directly applicable to this derivative. The response characteristic of NTA-trisilyl ester was 2,200 mm^2 peak area per microgram of NTA at maximum sensitivity of the hydrogen flame ionization detector. Accordingly, gas chromatography has the potential for detecting NTA concentrations of practical interest, providing suitable NTA isolation techniques can be developed.

The cupric ion-selective electrode provides the basis for a sensitive electrochemical detector for NTA. Apparatus for the on-stream determination of uncomplexed NTA has been developed. This may be used for determination of total NTA, after the latter is separated from bound metal ions and other complexing agents by a suitable means, such as ion-exchange chromatography.

Polarographic studies have shown that the bismuth-NTA complex is a suitable method for the determination of NTA in most waters. While some metal ions may interfere, a pre-electrolysis step and/or a standard addition technique seems feasible to eliminate this problem.

Potentiometric titration with cupric ion should provide a rapid and reliable referee method for the determination of NTA in detergent formulations. Such a method would appear to be superior to the spectrophotometric methods presently used, since the latter are affected by turbidities which are encountered in many of the samples.

SECTION II

RECOMMENDATIONS

The present study has identified three analytical techniques that can provide the basis for the development of sensitive methods for the determination of nitrilotriacetic acid at trace levels of concentration. Gas chromatography has great sensitivity, but its application depends upon the development of techniques for separation of NTA from the water matrix. The cupric ion-selective electrode may be used for chelometric trace determinations, but an ion-exchange step to de-complex the NTA and to separate it from other complexing agents is a prerequisite. Polarography has considerable utility but it can also be improved by a suitable pre-treatment procedure. Accordingly, the following recommendations are made for further investigation:

1. Investigation of non-aqueous separation techniques that would permit utilization of the gas chromatographic measurement of NTA-trisilyl ester for trace analytical purposes.

2. Investigation of simple ion-exchange processes for separation of NTA as the free acid, as a preliminary step for analysis by the cupric ion-selective electrode technique. The object of the study would be to develop on-stream methodology for which the technique is particularly applicable and for which the flow-cell designed in the present work is directly utilizable.

3. Further investigation of pre-electrolysis as a technique for removal of interfering ions, to extend the usefulness of polarographic NTA determinations.

4. A study in-depth of the promising potentiometric titration procedure to develop a referee method for the determination of NTA in detergent formulations.

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SECTION III

INTRODUCTION

The constituents of household detergents are potentially one of the largest sources of water pollution. Unless such substances are readily biodegradable or easily removable from water by conventional waste-treatment methods, they may accumulate to undesirable levels. Accordingly, it is imperative that reliable analytical methodology is available to monitor the concentrations of such substances in waste water, before and after treatment, and to identify residual levels that may accumulate. Without the capability of adequate analytical surveillance, deleterious if not dangerous conditions could ensue.

The proposed use of nitrilotriacetic acid as a builder in detergents is a case in point. While there are presently several methods for the determination of this material, each has its short comings for such reasons as complexity, cost, or time requirements. Furthermore, most of these have not been in use for a sufficient time that their reliability has been fully evaluated under practical conditions.

It was the purpose of this work to investigate several approaches to the problem of the determination of NTA in waste water. Techniques selected for this study include: gas chromatography; polarography; potentiometric titrimetry; and ion-selective electrode potentiometry. The studies were directed principally to the detection of residual levels in waste water. Consideration was given to the potential for development of monitoring techniques. A portion of this work was directed toward the problem of determination of NTA in detergent formulations by potentiometric titration.

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SECTION IV

GAS CHROMATOGRAPHIC STUDIES

The investigation of gas chromatography as a technique for the detection and analysis of NTA was undertaken from the following points of view:

1. Optimization of the analytical conditions for the elution, detection, and measurement of NTA.

2. Preparation of a suitable NTA derivative for analysis by gas chromatography and verification of its structure.

3. Determination of detector response and its linearity for NTA.

4. Preliminary investigation of recovery of NTA from aqueous media.

The gas chromatograph analysis system is shown in Fig. 1. The system was initially optimized in terms of helium carrier gas, hydrogen, and air flow rates. Conditions for analysis were then set as follows:

Chromatographic column: 6 ft by 0.25 in o.d. stainless steel tube packed with 10 percent w/w of UC-W98 silicone on 80-100 mesh acid washed, silane treated Chromosorb W.

Detector: Hydrogen Flame ionization

Electrometer: Six input range and eight output attenuation positions, provided an output signal of 1×10^{-12} amps at maximum sensitivity.

Column temperature: 180 ^{0}C ± 1 ^{0}C

Column effluent flow rate: 65 cm^3/min of helium

Hydrogen flow rate to jet: 45 cm^3/min

Air flow rate to detector: 220 cm^3/min

Injection port temperature: 240 ^{0}C

Detector temperature: 240 ^{0}C

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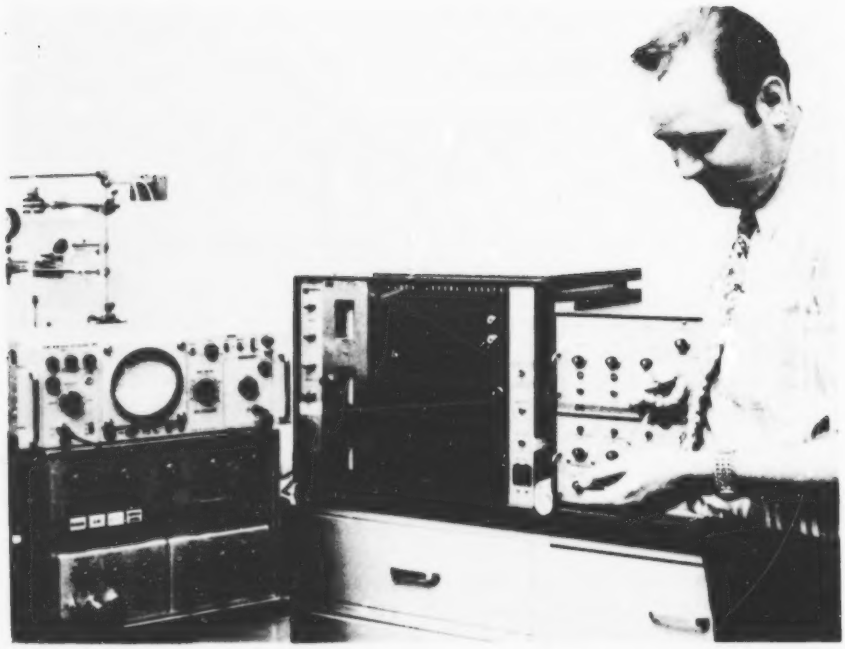


Figure 1. Gas Chromatograph used in the analysis.

An earlier gas chromatography study [1] of the contamination of EDTA by NTA demonstrated that the formation of NTA silyl ester may be accomplished by the reaction of free NTA with N,O-bis(trimethylsilyl)acetamide (BSA). The reaction is as follows:

$$CH_3C(=NSi(CH_3)_3)OSi(CH_3)_3 + N(CH_2COOH)_3 \rightarrow N(CH_2COOSi(CH_3)_3)_3$$

The reaction time was investigated and it was found that heating the reaction mixture of NTA in 0.1 cm^3 BSA under mild reflux for five minutes under a dry nitrogen atmosphere produced quantitative conversion of NTA to the ester form. Since BSA will react with moisture, anhydrous conditions were maintained during derivative formation, as indicated in Fig. 2. The BSA reagent was stored in a septum-sealed vial under refrigeration and withdrawn for use by penetrating the septum with a needle attached to a dry syringe. Prior to the addition of BSA, the system was thoroughly purged with dry nitrogen, and a magnesium perchlorate drying tube was attached to the top of the reflux condenser.

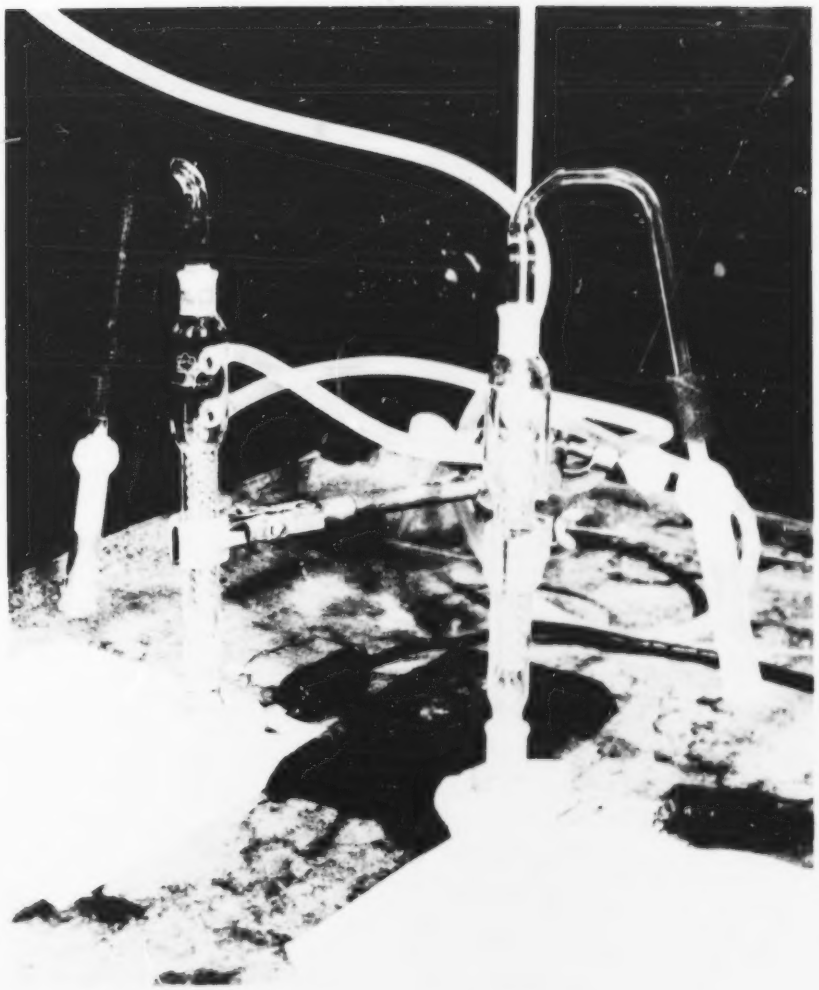
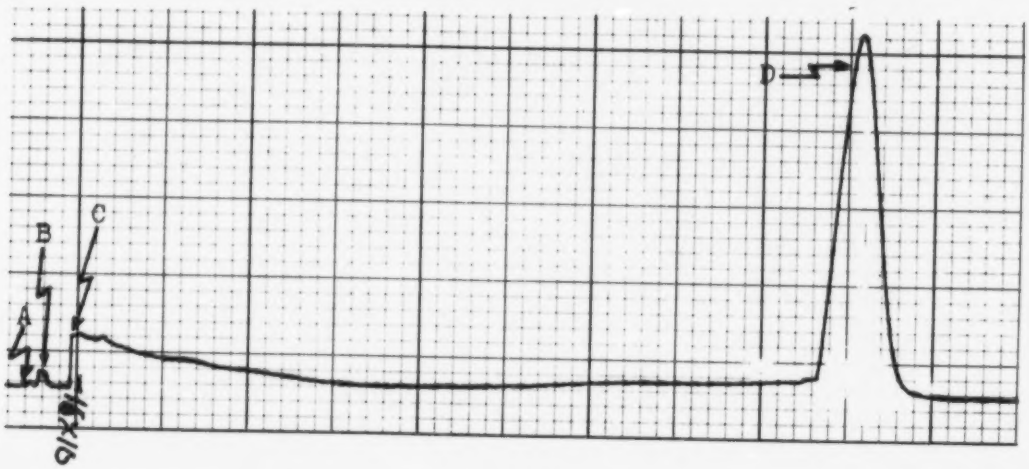


Figure 2. Derivatization of nitrilotriacetic acid.

A gas chromatogram of the eluted NTA ester is shown in Fig. 3. It was important to determine the structural authenticity of the eluted peak. To accomplish this a gas chromatograph-mass spectrometry (GC-MS) detection system (Fig. 4) was used. Fig. 5 represents the mass spectrum of the eluted peak with relative intensities greater than 1 percent of the parent ion. The presence of an ion current at mass number 407 (shown in the insert in the figure) substantiates the identity of the chromatographic peak as tris(trimethylsilyl)NTA ester. This fact, together with the GC-MS observation that no lower

NTA silyl ester appears at any point in the elution stream, confirms that the derivatization reaction occurs stoichiometrically to form the totally esterified derivative. The ion currents at masses 392 and 364 represented the parent ion minus one and three methyl groups, respectively. There was no ion current at 334, confirming the absence of a disilyl ester derivative. The highest current (base peak) occurred at mass number 73, representing the trimethylsilyl fragment.



A. Inject sample at high recorder attenuation
B. Solvent peak at high recorder attenuation
C. Switch to lower attenuation
D. NTA peak

Figure 3. Gas chromatogram of tri-ester derivative.

Nitrilotriacetic acid as present in water streams and beds may be present in the chelated form. Chau [2] has stated that some of the metal ions which strongly complex with NTA are Fe^{3+}, Ni^{2+}, and Cu^{2+}. In addition to this problem, fatty acids and hydrocarbons are included among candidate interfering chemicals which occur in water streams. In regard to the latter complication, the elution of hydrocarbon contaminants from a polar gas chromatographic column would occur very rapidly, long before the elution of NTA tri-ester. The retention comparison of long-chain fatty acids with that of NTA tri-ester on the relatively non-polar silicone column is shown in Table 1. Silylated myristic acid ($C_{17}H_{36}O_2Si$) would present the most troublesome species, yet does not

interfere with NTA measurement at concentrations below 10 times that of NTA. In severe cases of myristic acid contamination, it is suggested that steps be taken to isolate the NTA, or provide for selective NTA measurement. A mass spectrometer represents a detector which can be used for this purpose.

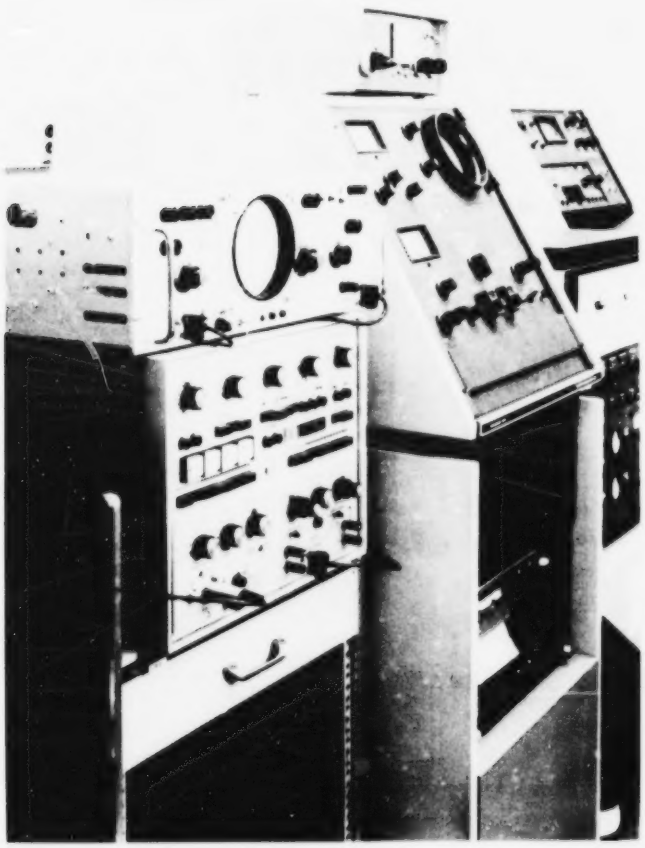


Figure 4. Gas chromatography-mass spectrometry system.

Considering the problem of NTA chelation with metal ions, it has been determined that recoveries from aqueous solution as assayed by the gas chromatographic procedure run below 40 percent, with the exception of Na^+. It was observed that when aqueous solutions containing Fe^{3+}, Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Na^+, K^+ and NTA were adjusted to pH 3 and were taken to dryness, NTA was not recovered. A critical point in the evaporation step is reached as dryness is approached. When

samples were taken past dryness, substantial losses of NTA occurred. Even under ideal conditions, the concentration of water samples without prior removal of metal ions effects low recoveries of NTA. The recovery of NTA added to Potomac River water was less than 3 percent.

Additional investigation of NTA isolation from chelated metal ions is essential. Longman [3] has reported that a chelating resin (Chelex 100) in the Na^+ form has a high affinity for metals chelated with NTA. The recovery of NTA from metal-free aqueous media may be enhanced by taking the final concentration to about 0.1 ml rather than to dryness, and introducing 1.5 ml of BSA.

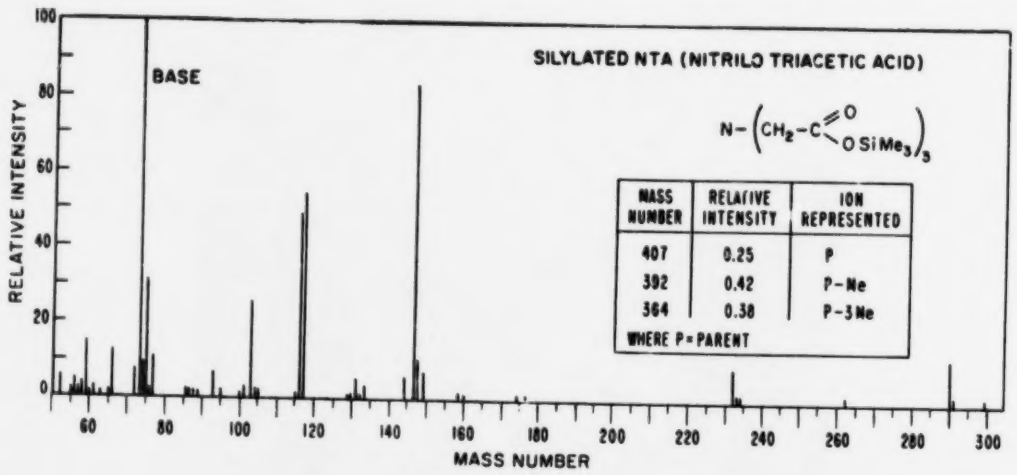

SILYLATED NTA (NITRILO TRIACETIC ACID)
BASE
RELATIVE INTENSITY
MASS NUMBER
MASS NUMBER | RELATIVE INTENSITY | ION REPRESENTED
407 | 0.25 | P
392 | 0.42 | P-Me
364 | 0.38 | P-3Me
WHERE P = PARENT

Figure 5. Mass spectrum of silylated NTA.

Table 1

Retention Times Comparison of Silylated NTA and Fatty Acids

Silylated Compound	Formula	Retention Time (minutes)
Decanoic acid	$C_{13}H_{28}O_2Si$	2.3
Lauric acid	$C_{15}H_{32}O_2Si$	4.6
NTA	$C_{15}H_{33}O_6NSi_3$	10.2
Myristic acid	$C_{17}H_{36}O_2Si$	11.2
Palmitic	$C_{19}H_{40}O_2Si$	22.6
Linoleic acid	$C_{21}H_{40}O_2Si$	48.8

The chromatographic conditions of operation were detailed above. For the determination of the level of detector response and its linearity, standard solutions of NTA were prepared by reacting known amounts of NTA with BSA, followed by dilution with carbon disulfide. The standard solutions were stored in septum-capped vials for gas chromatographic analysis.

Measured aliquots were withdrawn through the septa with a 10 µl syringe containing a few µl of carbon disulfide next to the plunger, followed by a few µl of air. The syringe contents were injected into the inlet port of the gas chromatograph using the carbon disulfide plug to flush the entire NTA sample into the column. The carbon disulfide and excess BSA reagent eluted within 1.5 minutes following injection. The trisilyl NTA ester emerged at 10.2 ± 0.1 minutes. The NTA standard solutions covered a sample injection weight range of 0.22 to 23.5 µg, expressed as free NTA. The response curve is given in Figure 6 in terms of mm^2 peak area for the NTA tri-ester peak as a function of sample weight of free NTA. The nominal response was 2,200 mm^2 peak area per µg of NTA, corrected to maximum detector sensitivity. This refers to a peak height above base of 30 percent of full scale deflection on a 10 mV recorder at an unattenuated electrometer input range of 10 for one microgram of NTA.

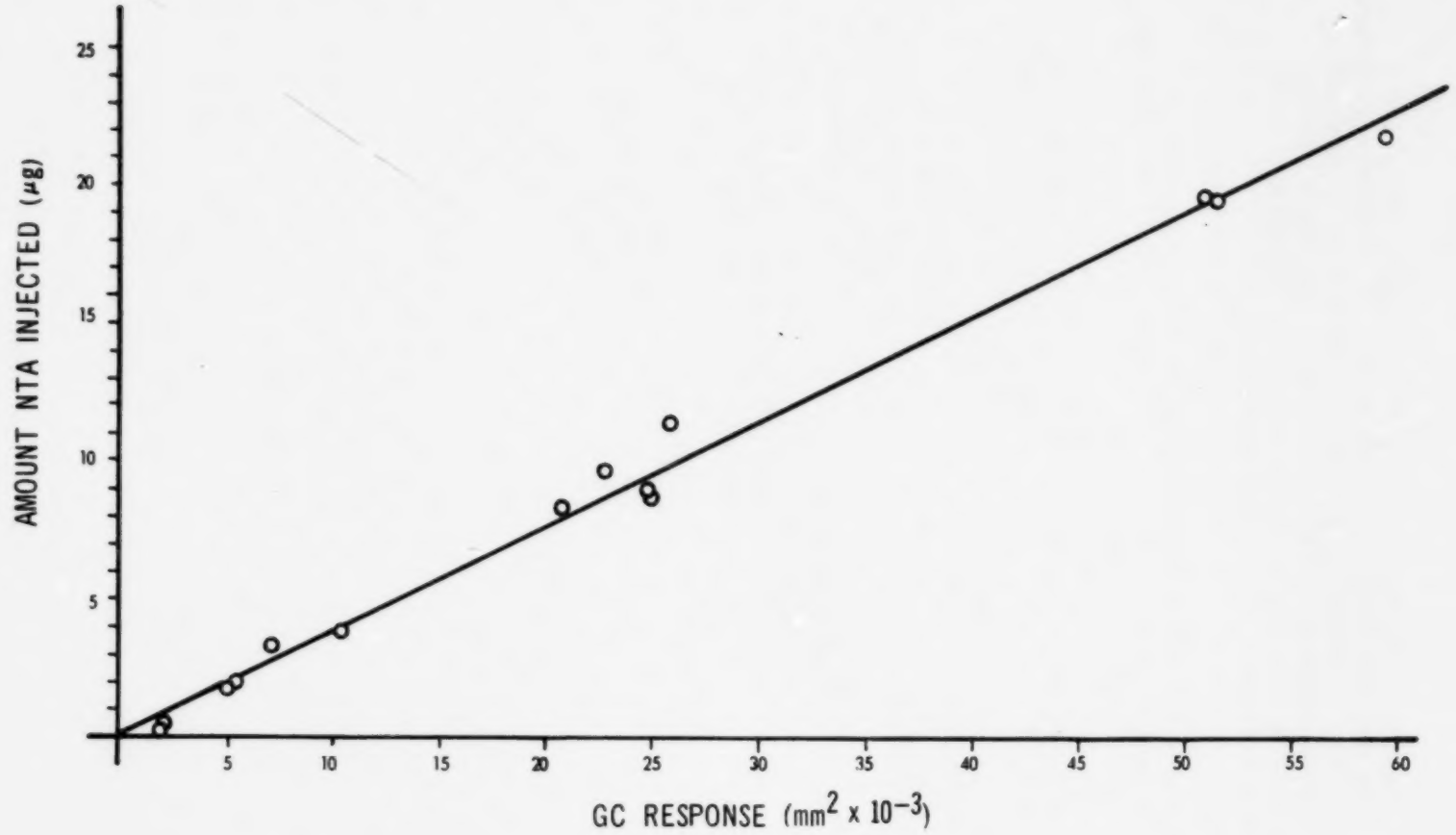


Figure 6. Gas chromatographic response for NTA.

SECTION V

ION-SELECTIVE ELECTRODE STUDIES

An electrochemical detector based on the cupric ion-selective electrode has been developed for the determination of complexing agents, such as NTA, EDTA, *etc.*, after separation by ion-exchange chromatography. This detector was developed independently of the separation method, and the evaluation of its response to NTA in the final system must await completion of the chromatographic method.

The detector system, shown in Figures 7 and 8 and diagrammed in Figure 9, is based on the response of a cupric ion-selective electrode to electrochemically generated cupric ion in a continuous, flow-through cell arrangement. In principle, the detector system operates in this way: (1) cupric ion is generated coulometrically at a constant rate upstream from the detector, *i.e.*, between the outlet of the chromatographic column and the detector; (2) the rate of generation is continuously variable to obtain optimum response at the detector depending upon the concentration of the complexing agents; (3) the detector assembly, described in detail below, produces a constant emf output until the cupric ion level is perturbed by complexation with NTA or some other ligand; (4) since the electrode only responds to the uncomplexed cupric ions, the magnitude of the emf change can be related to the degree of complexation and consequently to the amount of complexing agent present.

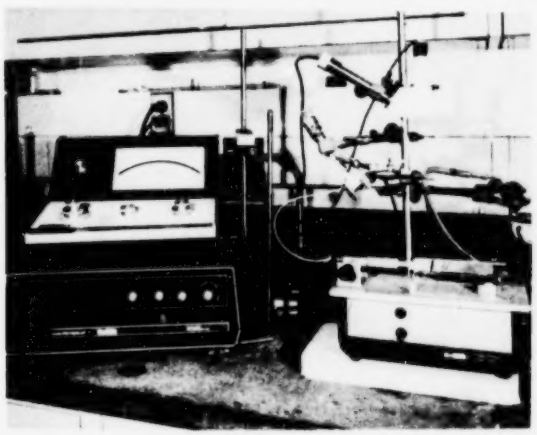


Figure 7. General view of ion-selective electrode apparatus.

The detector assembly consists of a flow chamber machined from Teflon into which is mounted the cupric ion-selective electrode and a reference electrode designed for use in flow assemblies. The indicator electrode is held securely in place by the aluminum holder attached to the Teflon assembly as shown in Figures 7, 8, and 9. This holder permits the electrode to be seated tightly against the flow chamber lip, thus preventing solution leakage around the electrode tip. The cupric ion indicator electrode is mounted 60° from the vertical to avoid bubble entrapment in the flow chamber which could cause spurious response.

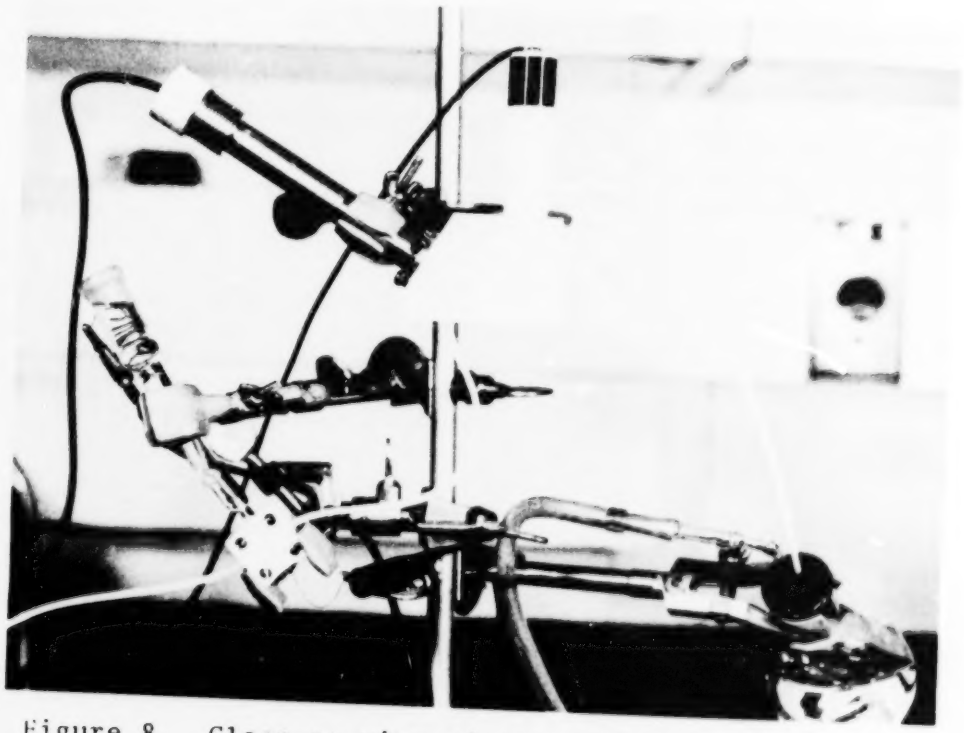


Figure 8. Close-up view of ion-selective electrode detector.

In order to test the response characteristics of this system, an electrolyte solution (0.01 M KNO_3) was flowed through the generator and detector assemblies at constant rate (0.4 ml/min) using a syringe pump (Figure 7). A constant current was applied to the coulometric cupric ion generator. From a knowledge of the flow rate and current, the concentration of cupric ion generated could be calculated and a working curve established for the electrode system. This curve, is linear from 5 ppm to about 0.2 ppm with a response slope of approximately 21 mV/pCu (theoretical: 29.5 mV/pCu). The response time of the electrode system to achieve a stable emf reading was measured for step changes in the generator current, *i.e.*, the cupric ion activity. In general, at the very dilute cupric ion levels generated (0.1 to 5 ppm), the time required to

establish an equilibrium emf was about 3-4 minutes. Calibration of the electrode system in stirred standard solutions showed similar behavior, *i.e.*, equilibration times of several minutes and a sub-Nernstian response slope of approximately 23 mV/pCu. At higher cupric ion concentrations, the electrode response is faster and more Nernstian.

The chromatographic procedure will require the removal of divalent cations from the complexing ligands, perhaps using a cation exchanger in the hydrogen ion form, followed by conversion of the acid-form ligands to their sodium salts by passage through another cation exchanger in the sodium form. This procedure would result in a sample of the proper characteristics to be determined by the cupric ion electrode detector.

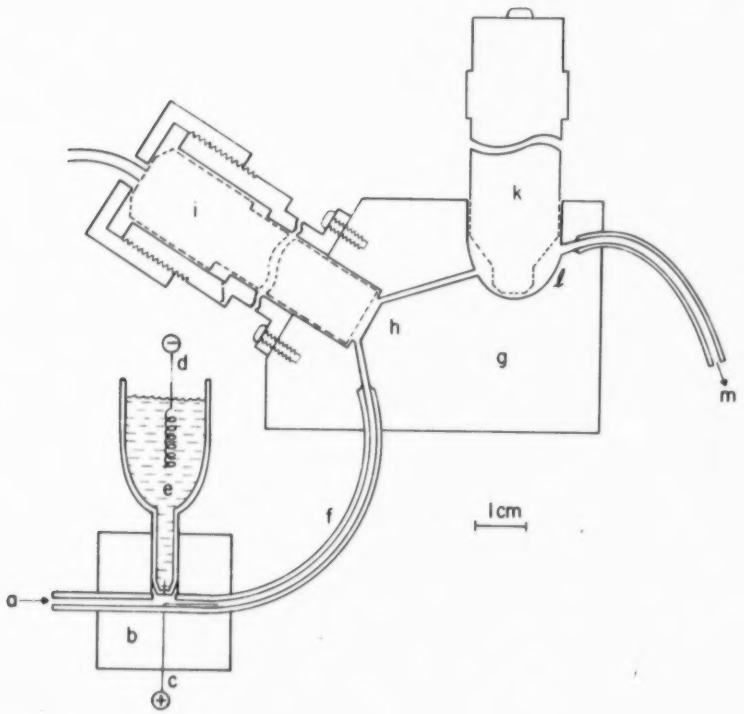


Figure 9. Diagrammatic view of ion-selective electrode detector.

SECTION VI

POLAROGRAPHIC STUDIES

A number of polarographic methods for the determination of NTA have been reported, most of them involving the addition of an excess of metal ion and measurement of the reduction peak of the metal-NTA complex. Daniel and LeBlanc utilized addition of excess cadmium ion at a pH of 7-10 to determine NTA in EDTA by conventional d.c. polarography [4,5]. Farrow and Hill modified the method somewhat using standard additions of the Cd-NTA complex and single cell cathode ray polarography [6]. Haberman determined traces of NTA in river water and sewage by the addition of excess indium and measurement of the In-NTA reduction peak [7]. To increase the sensitivity and reduce interferences, he used both cation and anion exchange column separations. Afghan and Goulden have developed methods for the determination of traces of NTA in water by measurement of either the Pb-NTA complex or the Bi-NTA complex [8,9]. The method using the Bi-NTA complex has been adapted by Gahler of the Water Quality Office, Pacific Northwest Laboratory, Corvallis, Oregon, for the determination of NTA in sea water [10], and by the Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada, for the determination of NTA in water [11].

Preliminary studies were conducted involving the lead, the cadmium and the bismuth complexes to determine which gave the best defined polarographic peaks. Indium was not considered as Afghan [9] reports that very high concentrations of indium are necessary for complete NTA recovery and at a mole ratio of 5:1 of In:NTA, the polarographic peak of the indium-NTA complex is extremely difficult to measure owing to its proximity to the indium reduction peak. The Pb-NTA complex was investigated in 3 different buffer systems: tris hydrochloride-ammonium hydroxide, glycine-ammonium hydroxide, and ammonium chloride-ammonium hydroxide, around pH 7-8. The Cd-NTA complex was also measured in an ammonium chloride-ammonium hydroxide buffer system at pH about 9. The Bi-NTA complex was then investigated in NaCl media at pH 2 and appeared to give the best defined peaks and the highest peak height for a given concentration of NTA. Plots of current-*vs*-concentration were linear. A slope of about 0.1 μA/ppm was found, with the instrumentation and electrodes used.

Aliquots of the supernatant liquid of several portions of river-bottom mud which had been equilibrated with NTA solutions for about a month to give final concentrations of 10 and 20 ppm of NTA were then analyzed. The river-bottom mud solution contained about 5 percent solids. Values of 5.2 and 10.3 ppm of NTA were obtained, showing recoveries of only about 50 percent. The original NTA solutions used to prepare the sludge mixtures were then analyzed to determine if the

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solution composition had changed. Values of 9.5 and 18.9 ppm were obtained showing good agreement with the 10 and 20 ppm starting compositions. It was postulated that part of the NTA had equilibrated with the sludge, which then settled to the bottom.

Several calibration curves in the region from 0.2 to 1.0 ppm of NTA were then run on different days.

The recommended procedure for the preparation of the calibration curves was essentially that developed by Afghan and Goulden [8,9] and recommended by Traversy [11]. This utilized a differential cathode ray polarograph in the subtractive mode of operation. Procedure: Aliquot 0.0, 1.0, 2.0, 3.0, 4.0, 5.0 ml of standard NTA solution (10 mg/l) into 50-ml beakers. Add 5 ml of 1N HCl to the blank. Add 4.5 ml of 1N HCl to each of the other solutions. Add 1 ml of 1 percent hydroxylamine hydrochloride to each beaker to reduce any iron present, then add 0.5 ml of bismuth solution (0.2 mg Bi/ml in 1M HCl). Add 25 ml of distilled water to each, adjust the pH to 2.0 with ammonium hydroxide and dilute the solutions to 50 ml in a volumetric flask. Add about 1 ml of mercury to each polarographic cell and transfer the solutions to the cells. The blank solution is placed in the right hand cell position, and a sample solution in the left hand cell position. Deaerate with nitrogen for 10 minutes, then measure the Bi-NTA polarographic peak at about -0.25V *vs* a mercury pool anode.

Some tap water solutions were also measured, but generally erratic and incomplete NTA recovery was obtained. An interfering peak, believed to be copper or ferric ion which had not been successfully reduced, appeared close to the rising portion of the Bi-NTA peak making reproducible measurement of the Bi-NTA difficult. Although the solutions were measured subtractively with a tap water blank in the second cell, it was not possible to balance out the base lines.

Gahler [10] found that as little as 2 ppm of copper in water causes very high results. At first this seemed to be inconsistent with the above findings. Then it was realized that he had used a low resolution conventional polarograph which would present the Cu-Bi-NTA peak as a single peak. The cathode ray polarograph separates the two peaks, but the Bi-NTA peak follows the interfering peak so closely that a diffusion level plateau from which to measure the base line is not reached.

In view of the fact that the chromatographic separation of NTA might not be feasible, it seemed possible that interfering metals ions could be separated by electrolysis of an acidified solution of the tap water for several hours at -0.9V. Preliminary efforts showed this to be feasible.

Although NTA is reported to form complexes with few metal ions commonly present in tap water at pH 2, except bismuth, the possibility exists that incomplete NTA recovery from tap water could result from its reacting with some other species in the water. This effect could probably be overcome by a standard addition technique. A set of tap water samples was taken through the procedure as described above, except 4 ml of additional NTA was added to each solution including the blank. The recovery was quantitative, except for the 0.2 ppm level.

Sufficient instrumental sensitivity is available so that as little as 0.05 ppm of NTA in the final solution could be readily determined. This is the equivalent of 0.1 ppm in the original water sample, however usually sufficient water sample is available for preconcentration making possible the determination of even lower levels of NTA.

In conclusion, it appears that the polarographic determination of NTA as the Bi-NTA complex is a suitable method. However, if the chromatographic separation of the NTA is not performed, a pre-electrolysis step and/or the standard addition technique may be necessary.

SECTION VII

POTENTIOMETRIC TITRATION STUDIES

The potentiometric titration method described by Siggia, *et al.* [12] was investigated for its applicability to the determination of NTA in detergents.

Titrations were performed in a 1:1 solvent mixture of water and pyridine, using a platinum-calomel electrode system. Microliter quantities of the 0.1M copper nitrate titrant were added by means of a "Micrometric" syringe. Equilibrium was readily established by magnetic stirring. Amounts of NTA in the range of 0.5-5 mg in 10 ml of the mixed solvent gave sharp, readily discernible end-points. Assuming a 1:1 Cu-NTA complex, commercial samples of NTA and Na_2NTA invaribly assayed 99-100 percent.

Several brands of commercial detergents were analyzed for NTA by the above procedure. Typical results are given in Table 2.

Table 2. Apparent NTA Content of Various Detergents

Detergent[a]	Wt. % NTA
Brand CH	8.1
Brand T	<0.5
Brand CA[b]	(∿8)
Brand DP[c]	<0.5
Sample 18-135	11.4
Sample 26-184	5.7

[a] 50-mg samples taken for analysis

[b] gave a reverse titration curve relative to all other samples and standards

[c] label claimed phosphate- and NTA-free

The results given in Table 2 should be considered only as preliminary values. Although known amounts of NTA were recovered when added to the detergent samples, the varying shapes of the titration curves from detergent to detergent require further study and understanding. As an extreme example the titration curve for one detergent, which is

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undoubtedly high in phosphate, exhibited a negative rather than positive break at what was considered to be the end-point. The titration curves for all other samples, however, were similar to those obtained for the standards.

With further study, it is felt that a potentiometric titration with Cu^{+2} could afford a rapid and reliable reference method for determining NTA in detergents. Spectrophotometric procedures, although briefly examined in the early stages of this investigation, do not appear as generally applicable because of the turbidities which are encountered with many of the samples.

SECTION VIII

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Gas Chromatographic Studies - Walter L. Zielinski, Jr. and William D. Dorko

Ion-Selective Electrode Studies - Richard A. Durst

Polarographic Studies - E. June Maienthal and B. T. Duhart.

Potentiometric Titration Studies - Robert W. Burke and Robert Deardorff.

Dr. David H. Freeman directed the gas chromatographic studies. Dr. John K. Taylor served as coordinator of activities and prepared the final report.

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SECTION IX

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27 Abstract

A gas chromatographic method has been developed for the determination of NTA, after esterification of the isolated free acid form with N,O-bis(trimethylsilyl)acetamide.

The cupric ion selective electrode provides the basis for a sensitive electrochemical detector for NTA. Apparatus has been developed for the on-stream determination of uncomplexed NTA. After the latter is separated from bound metal ions and other complexing agents by a suitable means, such as ion-exchange chromatography.

Polarographic measurement of the bismuth-NTA complex is suitable for the determination of NTA in most waters. A pre-electrolysis step and/or a standard addition technique seems feasible to eliminate interference problems.

Potentiometric titration with cupric ion provides a rapid and reliable referee method for the determination of NTA in detergent formulations and when turbidities are encountered in samples.

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